

# Double deboronation and homometalation of 1,1'-bis(*ortho*-carborane) †§

Gobika Thiripuranathar, Antony P. Y. Chan, Dipendu Mandal, Wing Y. Man, Mario Argentari, Georgina M. Rosair and Alan J. Welch\*

## Abstract

Double deboronation of 1,1'-bis(*ortho*-carborane) results in a mixture of racemic and meso diastereoisomers which are sources of the  $[7-(7'-7',8'-nido-C_2B_9H_{10})-7,8-nido-C_2B_9H_{10}]^{4-}$  tetraanion. Consistent with this, metalation of the mixture with  $\{Ru(p\text{-cymene})\}$  affords the diastereoisomers  $\alpha$ -[1-(8'-2'-(*p*-cymene)-2',1',8'-*closo*- $RuC_2B_9H_{10}$ )-3-(*p*-cymene)-3,1,2-*closo*- $RuC_2B_9H_{10}$ ] (**3 $\alpha$** ) and  $\beta$ -[1-(8'-2'-(*p*-cymene)-2',1',8'-*closo*- $RuC_2B_9H_{10}$ )-3-(*p*-cymene)-3,1,2-*closo*- $RuC_2B_9H_{10}$ ] (**3 $\beta$** ) in which the primed cage has undergone a spontaneous 3',1',2' to 2', 1',8'- $RuC_2B_9$  isomerisation. Analogous cobaltacarboranes  $\alpha$ -[1-(8'-2'-Cp-2',1',8'-*closo*- $CoC_2B_9H_{10}$ )-3-Cp-3,1,2-*closo*- $CoC_2B_9H_{10}$ ] (**4 $\alpha$** ) and  $\beta$ -[1-(8'-2'-Cp-2',1',8'-*closo*- $CoC_2B_9H_{10}$ )-3-Cp-3,1,2-*closo*- $CoC_2B_9H_{10}$ ] (**4 $\beta$** ) are formed by metalation with  $CoCl_2/NaCp$  followed by oxidation, along with a small amount of the unique species [8-(8'-2'-Cp-2',1',8'-*closo*- $CoC_2B_9H_{10}$ )-2-Cp-2,1,8-*closo*- $CoC_2B_9H_{10}$ ] (**5**) if the source of the tetraanion is  $[HNMe_3]_2[7-(7'-7',8'-nido-C_2B_9H_{11})-7,8-nido-C_2B_9H_{11}]$ . Two-electron reduction and subsequent reoxidation of **4 $\alpha$**  and **4 $\beta$**  affords species indistinguishable from **5**. Reaction between  $[Ti]_2[1-(1'-3',1',2'-*closo*- $TiC_2B_9H_{10}$ )-3,1,2-*closo*- $TiC_2B_9H_{10}$ ] and  $[CoCpI_2(CO)]$  leads to the isolation of a further isomer of  $(CpCoC_2B_9H_{11})_2$ , *rac*-[1-(1'-3'-Cp-3',1',2'-*closo*- $CoC_2B_9H_{10}$ )-3-Cp-3,1,2-*closo*- $CoC_2B_9H_{10}$ ] (**6**), which displays intramolecular dihydrogen bonding. Thermolysis of **6** yields **4 $\alpha$** , allowing a link to be established between the  $\alpha$  and  $\beta$  forms of **3** and **4** and racemic and meso forms of the  $[7-(7'-7',8'-nido-C_2B_9H_{10})-7,8-nido-C_2B_9H_{10}]^{4-}$  tetraanion, whilst reduction-oxidation of **6** again results in a product indistinguishable from **5**.$

Institute of Chemical Sciences, Heriot-Watt University, Edinburgh, UK EH14 4AS. E-mail: [a.j.welch@hw.ac.uk](mailto:a.j.welch@hw.ac.uk); Tel: +44 (0)131 451 3217

† In memory of Professor Igor T. Chishevsky.

§ Electronic supplementary information (ESI) available: NMR spectra of all new compounds reported. Details of the disorder in  $[BTMA]_2[1]$ . CCDC 1516771-1516778. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/xxxxxxxxxx

## Introduction

The compound [1-(1'-1',2'-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)-1,2-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>], two *ortho*-carborane units connected by a C–C bond,<sup>1</sup> is commonly referred to as 1,1'-bis(*ortho*-carborane) (Fig. 1). First prepared in 1964,<sup>2</sup> the chemistry of 1,1'-bis(*o*-carborane) remained underdeveloped for long periods, in large part because of the lack of a reliable and high-yielding synthesis. That problem has now been overcome,<sup>3</sup> and recent years have witnessed an impressive blossoming of the chemistry of 1,1'-bis(*o*-carborane) in a number of diverse areas broadly classified as derivatisation,<sup>4-8</sup> cage expansion,<sup>9-11</sup> metalation,<sup>12-14</sup> bond activation<sup>15-18</sup> and the synthesis of luminescent complexes.<sup>19</sup>

<Fig. 1 near here>

In 2015 we reported the metalation of singly-deboronated 1,1'-bis(*o*-carborane) with both {Ru(*p*-cymene)} and {CoCp} fragments.<sup>13</sup> In both cases non-isomerised 3,1,2-MC<sub>2</sub>B<sub>9</sub>-1',2'-C<sub>2</sub>B<sub>10</sub> and isomerised 2,1,8-MC<sub>2</sub>B<sub>9</sub>-1',2'-C<sub>2</sub>B<sub>10</sub> products were isolated, and we explored the conversion of the former to the latter by both thermolytic and chemical means. In this contribution we extend that initial work to the homometalation of doubly-deboronated 1,1'-bis(*o*-carborane) which adds two interesting dimensions to the study: (i) double deboronation of 1,1'-bis(*o*-carborane) introduces the possibility of metallacarborane products which are diastereoisomers, and (ii) the presence of two metallacarborane clusters in the same molecule allows for products in which neither cage has isomerised, one cage has isomerised or both cages have isomerised.

Prior to the present study the only reported examples of metalation of doubly-deboronated 1,1'-bis(*o*-carborane) of which we are aware are two bis-rhodacarboranes, one of 3,1,2-RhC<sub>2</sub>B<sub>9</sub>-3',1',2'-RhC<sub>2</sub>B<sub>9</sub> form and the other of 3,1,2-RhC<sub>2</sub>B<sub>9</sub>-2',1',8'-RhC<sub>2</sub>B<sub>9</sub> form, afforded by the reaction between [Cs]<sub>2</sub>[7-(7'-7',8'-*nido*-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-7,8-*nido*-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] and [Rh(COD)(PEt<sub>3</sub>)Cl].<sup>20</sup>

## Results and discussion

### Double deboronation of 1,1'-bis(*o*-carborane)

The single and double deboronations of 1,1'-bis(*o*-carborane) were first reported by Hawthorne *et al.* in 1971.<sup>21</sup> Double deboronation was achieved by heating to reflux 1,1'-bis(*o*-carborane) and five equivalents of KOH in EtOH for 120 h, isolating the product as both [Cs]<sup>+</sup> and [HNMe<sub>3</sub>]<sup>+</sup> salts. We have found that acceptable yields of product are achieved in considerably less time (18-48 h) by using of larger amounts of KOH (typically 25-30 equivalents). The doubly-deboronated product has been isolated as the [HNMe<sub>3</sub>]<sup>+</sup>, [BTMA]<sup>+</sup> and [Tl]<sup>+</sup> salts ([BTMA]<sup>+</sup> = benzyltrimethylammonium, [C<sub>6</sub>H<sub>5</sub>CH<sub>2</sub>NMe<sub>3</sub>]<sup>+</sup>). Note, however, that these are described in different ways because in the [HNMe<sub>3</sub>]<sup>+</sup> and [BTMA]<sup>+</sup> salts each

cage is protonated to afford a double nido dianion whilst for the  $[\text{Ti}]^+$  salt the cages are not protonated and we assume that one Ti atom is weakly associated with each carborane cage (now formally *closo*) in the same way as has been confirmed for  $[\text{Ti}][\text{TiC}_2\text{B}_9\text{H}_{11}]$ .<sup>22</sup> Thus the  $[\text{HNMe}_3]^+$  and  $[\text{BTMA}]^+$  salts are salts of  $[\text{7}-(\text{7}'\text{-7}',\text{8}'\text{-nido-C}_2\text{B}_9\text{H}_{11})\text{-7,8-nido-C}_2\text{B}_9\text{H}_{11}]^{2-}$ ,  $[\text{HNMe}_3]_2[\mathbf{1}]$  and  $[\text{BTMA}]_2[\mathbf{1}]$ , respectively, whilst the  $[\text{Ti}]^+$  salt is  $[\text{Ti}]_2[\text{1}-(\text{1}'\text{-3}',\text{1}',\text{2}'\text{-closo-TiC}_2\text{B}_9\text{H}_{10})\text{-3,1,2-closo-TiC}_2\text{B}_9\text{H}_{10}]$  ( $[\text{Ti}]_2[\mathbf{2}]$ ). In metalation reactions all three salts are potential sources of the  $[\text{7}-(\text{7}'\text{-7}',\text{8}'\text{-nido-C}_2\text{B}_9\text{H}_{10})\text{-7,8-nido-C}_2\text{B}_9\text{H}_{10}]^{4-}$  tetraanion, but for practical purposes  $[\text{HNMe}_3]_2[\mathbf{1}]$  and  $[\text{Ti}]_2[\mathbf{2}]$  are the most useful.

The insolubility of  $[\text{Ti}]_2[\mathbf{2}]$  in common solvents meant that it was characterised only by elemental analysis, whilst the more soluble species  $[\text{HNMe}_3]_2[\mathbf{1}]$  and  $[\text{BTMA}]_2[\mathbf{1}]$  were also characterised by  $^{11}\text{B}$  and  $^1\text{H}$  NMR spectroscopy.

Double deboronation of 1,1'-bis(*o*-carborane) potentially affords both racemic and meso diastereoisomers (Fig. 2). Although Hawthorne and co-workers recognised this possibility they suggested that the meso form would be more stable and hence more likely to form.<sup>21</sup> No evidence for diastereoisomers was afforded by the 80 MHz  $^{11}\text{B}$  NMR spectrum of the  $[\text{Cs}]^+$  salt but, in contrast, we see a clear indication of two such isomers from the 128.4 MHz  $^{11}\text{B}\{^1\text{H}\}$  spectra of  $[\text{HNMe}_3]_2[\mathbf{1}]$  and  $[\text{BTMA}]_2[\mathbf{1}]$  (Fig. 3), with minor resonances at  $\delta$  -17.6, -21.3 and -24.4 close to major resonances at  $\delta$  -18.5, -20.4 and -23.8, respectively. Very approximately, the ratio of major:minor isomers is *ca.* 2:1 (this is supported by the relative integrals of two resonances assigned to  $\text{C}_{\text{cage}}\text{H}$  in the  $^1\text{H}$  NMR spectra), but it is not possible to determine which diastereoisomer is major and which is minor.

<Figs. 2 and 3 near here>

Frustratingly, a single-crystal diffraction study of  $[\text{BTMA}]_2[\mathbf{1}]$  did not resolve this question because of disorder. The anion is located on a crystallographic inversion centre at the mid-point of the C7–C7' bond. Within each cage there is disorder between vertices 8 and 11 (meaning that the ion cannot be described as simply racemic or meso; almost certainly both forms crystallise together) and there is further disorder with both vertices 8 and 11 not fully occupied and a partial ghost vertex, vertex 12, lying over the 7-8-9-10-11 face. The best crystallographic model of the disorder is that vertex 8 is 51%C+15%B, vertex 11 is 29%C+65%B and vertex 12 is 20%C+20%B. This implies that in the solid state more of the anion is in the meso form, and that is what is shown in the simplified representation in Fig. 4.

<Fig. 4 near here>

Thus the combined spectroscopic and crystallographic evidence implies that double deboronation of 1,1'-bis(*o*-carborane) results in a mixture of diastereoisomers, and this is supported by the results of metalation reactions described in the following sections.

## Ruthenacarboranes

Deprotonation of  $[\text{HNMe}_3]_2[\mathbf{1}]$  with *n*-BuLi in THF followed by addition of  $[\text{RuCl}_2(p\text{-cymene})]_2$  or, alternatively, direct reaction between  $[\text{Ti}]_2[\mathbf{2}]$  and  $[\text{RuCl}_2(p\text{-cymene})]_2$  in THF, affords the isomeric ruthenacarborane compounds  $\alpha$ -[1-(8'-2'-(*p*-cymene)-2',1',8'-*closo*- $\text{RuC}_2\text{B}_9\text{H}_{10}$ )-3-(*p*-cymene)-3,1,2-*closo*- $\text{RuC}_2\text{B}_9\text{H}_{10}$ ] ( $\mathbf{3}\alpha$ ) and  $\beta$ -[1-(8'-2'-(*p*-cymene)-2',1',8'-*closo*- $\text{RuC}_2\text{B}_9\text{H}_{10}$ )-3-(*p*-cymene)-3,1,2-*closo*- $\text{RuC}_2\text{B}_9\text{H}_{10}$ ] ( $\mathbf{3}\beta$ ) following isolation by both column and thin-layer chromatography (Scheme 1). Isolated yields by both methods are relatively poor but those from using  $[\text{Ti}]_2[\mathbf{2}]$  are somewhat better, 11% and 5% respectively.

<Scheme 1 near here>

The isomeric nature of  $\mathbf{3}\alpha$  and  $\mathbf{3}\beta$  was confirmed by elemental analysis and mass spectrometry, and the close relationship between their molecular structures was implied by the similarity of their NMR spectra. In terms of detailed information the  $^{11}\text{B}\{^1\text{H}\}$  NMR spectra of both are relatively uninformative with multiple overlapping resonances which are impossible to integrate with confidence. In contrast the  $^1\text{H}$  NMR spectra of both  $\mathbf{3}\alpha$  and  $\mathbf{3}\beta$  clearly show two sets of resonances assigned to *p*-cymene and two  $\text{C}_{\text{cage}}\text{H}$  resonances, implying that within each species the two ruthenacarborane cages are in different isomeric forms.

The precise natures of  $\mathbf{3}\alpha$  and  $\mathbf{3}\beta$  were established by crystallographic studies, and perspective views of single molecules are presented in Fig. 5 and Fig. 6, respectively. Compounds  $\mathbf{3}$  are diruthenacarboranes in which one cage (unprimed) has a 3,1,2- $\text{RuC}_2\text{B}_9$  architecture whilst the other (primed) is 2,1,8- $\text{RuC}_2\text{B}_9$ . Since compounds  $\mathbf{3}$  result from metalation of  $[\text{HNMe}_3]_2[\mathbf{1}]$  or  $[\text{Ti}]_2[\mathbf{2}]$  in which the C atoms in each cage are adjacent the 2',1',8'- $\text{RuC}_2\text{B}_9$  cage must arise from isomerisation following metalation. Importantly,  $\mathbf{3}\alpha$  and  $\mathbf{3}\beta$  are related as diastereoisomers – with the chiralities of the unprimed cages the same (as in Figs. 5 and 6) the chiralities of the primed cages are opposite. Clearly this arises from the fact that the bis-nido precursors  $[\text{HNMe}_3]_2[\mathbf{1}]$  and  $[\text{Ti}]_2[\mathbf{2}]$  exist as diastereoisomeric mixtures, and indeed it establishes that this must be so – whilst the anionic diastereomeric precursors could not easily be separated the neutral metallacarborane products are amenable to separation by chromatography. Note, however, that the terms racemic and meso cannot strictly be applied to the diastereoisomers of  $\mathbf{3}$  since the two metallacarborane components are different (one 3,1,2- $\text{MC}_2\text{B}_9$  the other 2',1',8'- $\text{MC}_2\text{B}_9$ ). Moreover we cannot easily associate either  $\mathbf{3}\alpha$  or  $\mathbf{3}\beta$  with a particular racemic or meso precursor (however, see later) since the mechanism of the isomerisation that affords the 2',1',8'- $\text{RuC}_2\text{B}_9$  cage remains unknown, so we use the descriptors  $\alpha$  and  $\beta$  to distinguish them.

<Fig. 5 near here>

<Fig. 6 near here>

Presumably the initial product when doubly-deboronated 1,1'-bis(*o*-carborane) is metalated with {Ru(*p*-cymene)} fragments is the 3,1,2-RuC<sub>2</sub>B<sub>9</sub>-3',1',2'-RuC<sub>2</sub>B<sub>9</sub> compound (as a diastereoisomeric mixture) which then undergoes spontaneous isomerisation of one cage from 3,1,2-RuC<sub>2</sub>B<sub>9</sub> to 2,1,8-RuC<sub>2</sub>B<sub>9</sub>. We recently showed that the singly-metalated species [1-(1'-1',2'-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)-3-(*p*-cymene)-3,1,2-*closo*-RuC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**I**) isomerises to [8-(1'-1',2'-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)-2-(*p*-cymene)-2,1,8-*closo*-RuC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] with mild heating (THF reflux),<sup>13</sup> and therefore it was of interest to discover if similar thermolysis of compounds **3** would effect isomerisation of the 3,1,2-RuC<sub>2</sub>B<sub>9</sub> cage. It does not. Both **3α** and **3β** are recovered unchanged (save for some decomposition) on heating to reflux in THF for 2.5 h.

Compound **I** was found to be sterically-crowded, with a pronounced bend-back of the *p*-cymene ligand away from the carborane cage attached to C1. Similar steric crowding is discernible in the 3,1,2-RuC<sub>2</sub>B<sub>9</sub> cages of **3α** and **3β**, not surprising since they are related to **I** by nominal replacement of the {C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>} substituent of **I** with {(*p*-cymene)RuC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>}. In **3α** and **3β** the bend-back of the *p*-cymene ligand on Ru3 with respect to the least-squares plane through the metal-bonded cage atoms C1C2B7B8B4 [by 17.6(2) and 17.7(3)° respectively] is clearly visible in Figs. 5 and 6. Further evidence of this intramolecular crowding is the observation that Ru–C1 is *ca.* 0.1 Å longer than Ru–C2. In contrast, in the 2',1',8'-RuC<sub>2</sub>B<sub>9</sub> cages of **3α** and **3β** there is no significant bend-back of the *p*-cymene ligand, which makes dihedral angles of only 3.1(2) and 2.7(3)°, respectively, with the least-squares plane through atoms C1'B6'B11'B7'B3'. We presume that in the 3,1,2-RuC<sub>2</sub>B<sub>9</sub>-3',1',2'-RuC<sub>2</sub>B<sub>9</sub> precursors of **3α** and **3β** both cages suffer steric congestion and that gaining partial relief from this is a contributory factor in the observed isomerisation.

### Cobaltacarboranes

Double deprotonation of [HNMe<sub>3</sub>]<sub>2</sub>[**1**] with *n*-BuLi followed by treatment with CoCl<sub>2</sub>/NaCp and finally aerial oxidation yields, on work-up involving preparative TLC, two mobile orange bands and a trace amount of a mobile yellow band (Scheme 2). Reaction between [Ti]<sub>2</sub>[**2**] and CoCl<sub>2</sub>/NaCp affords the same two orange products, in somewhat better yields, but no evidence for the yellow species. Elemental analysis and mass spectrometry imply that all three compounds are isomers of (CpCoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)<sub>2</sub>, *i.e.* both carborane cages have been metalated with {CoCp} fragments. Spectroscopically the two orange products are clearly very similar whereas the yellow species is quite different.

<Scheme 2 near here>

In the <sup>1</sup>H NMR spectrum of each of the orange products are two resonances assigned to Cp-*H* atoms (*ca.* 5.8 and 5.5 ppm) and two resonances assigned to C<sub>cage</sub>*H* atoms (*ca.* 4.1 and 2.8 ppm) the last pair suggesting that one cobaltacarborane cage is of 3,1,2-CoC<sub>2</sub>B<sub>9</sub> architecture and the other is of 2,1,8-CoC<sub>2</sub>B<sub>9</sub> architecture, by comparison with the C<sub>cage</sub>*H* resonances in [3-

Cp-3,1,2-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>]<sup>23</sup> and [2-Cp-2,1,8-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>11</sub>].<sup>12</sup> That the two cages are of different isomeric form is also supported by the relative complexities of the <sup>11</sup>B{<sup>1</sup>H} NMR spectra.

Single-crystal X-ray diffraction studies established that the orange products are, indeed, 3,1,2-CoC<sub>2</sub>B<sub>9</sub>-2',1',8'-CoC<sub>2</sub>B<sub>9</sub> species and that, as was the case with **3α** and **3β**, they are related as diastereoisomers. In Fig. 7 and Fig. 8 the unprimed 3,1,2-CoC<sub>2</sub>B<sub>9</sub> cages of α-[1-(8'-2'-Cp-2',1',8'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-Cp-3,1,2-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**4α**) and β-[1-(8'-2'-Cp-2',1',8'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-Cp-3,1,2-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**4β**) are drawn with the same chirality whilst in the primed 2',1',8'-CoC<sub>2</sub>B<sub>9</sub> cages the chiralities are different between α and β forms.<sup>24</sup> Note that the structure of **4β** was determined from two different crystals, one solvent-free and the other containing MeCN of solvation. The two structures are related by a simple twist of *ca.* 72° about the C1–C8' bond.

<Fig. 7 near here>

<Fig. 8 near here>

Similar to **3α** and **3β** the 3,1,2-CoC<sub>2</sub>B<sub>9</sub> cages in **4α** and **4β** suffer from intramolecular steric crowding, manifested by pronounced bend-back of the Cp ligand relative to the C1C2B7B8B4 plane [15.37(11)° in **4α**, 13.98(12)° in **4β** and 14.5(3)° in **4β**·MeCN] and Co–C1 connectivities *ca.* 0.1 Å longer than Co–C2 connectivities. In contrast there is no discernible bend-back of the Cp ligands in the 2',1',8'-CoC<sub>2</sub>B<sub>9</sub> cages [dihedral angles between Cp and C1'B6'B11'B7'B3' planes 2.81(11), 2.29(13) and 2.5(4)°, respectively].

In the <sup>1</sup>H NMR spectrum of **5**, the yellow co-product of **4α** and **4β** when [HNMe<sub>3</sub>]<sub>2</sub>[**1**] is the source of double deboronated 1,1'-bis(*ortho*-carborane), is a single Cp-*H* resonance and a single C<sub>cage</sub>*H* resonance, the chemical shift of the latter, δ 2.66 ppm, suggestive of a 2,1,8-CoC<sub>2</sub>B<sub>9</sub> isomer.<sup>12</sup> The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum of **5** is surprisingly simple with only six resonances resolved at 128.4 MHz, 1.1/-0.9 (total 8B), -5.7 (4B), -12.0 (2B) and -16.8/-18.0 (total 4B).

A crystallographic study (Fig. 9) confirmed that **5** is the symmetric species [8-(8'-2'-Cp-2',1',8'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-2-Cp-2,1,8-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>], the first example of a 2,1,8-MC<sub>2</sub>B<sub>9</sub>-2',1',8'-MC<sub>2</sub>B<sub>9</sub> derivative of 1,1'-bis(*ortho*-carborane) to be reported. The molecule has crystallographically-required C<sub>2h</sub> symmetry with vertices 1 and 11 (and 1' and 11') equally disordered between C and B. Consequently it is impossible to establish from crystallography if **5** is the racemic or meso diastereoisomer or a mixture of both.

<Fig. 9 near here>

Given that the [HNMe<sub>3</sub>]<sub>2</sub>[**1**] starting material is a mixture of racemic and meso forms it is reasonable to suggest that **5** should also be formed as a racemic-meso mixture, but only one yellow band is isolated by preparative TLC. In the racemic form of **5** the two cages would be both chemically and magnetically equivalent, giving rise to only one Cp-*H* and one C<sub>cage</sub>*H*

resonance, as observed. In the meso form the cages are chemically equivalent but magnetically inequivalent, potentially giving rise to two Cp-*H* and two C<sub>cage</sub>*H* resonances. However, what distinguishes racemic from meso C<sub>cage</sub>*H* arrangements (whether vertices 1 and 11 in the other cage are C or B) is six connectivities away whilst what distinguishes racemic from meso Cp-*H* is seven connectivities away, so it is certainly conceivable that the *effective* distinction could be lost and single resonances observed for the two Cp-*H* atoms and the two C<sub>cage</sub>*H* atoms in the meso isomer at the same chemical shifts as those in the racemic isomer.

This suggestion is supported by the results of redox experiments on **4α** and **4β**. We have previously shown that reduction of [1-(1'-1',2'-*closo*-C<sub>2</sub>B<sub>10</sub>H<sub>11</sub>)-3-Cp-3,1,2-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**II**) causes a 3,1,2- to 2,1,8- isomerisation of the CoC<sub>2</sub>B<sub>9</sub> cobaltacarborane cage.<sup>13</sup> Consequently compounds **4α** and **4β** were each separately reduced (two equivalents of sodium naphthalenide in THF) and then aerially oxidised. In both cases single yellow products with identical (within error) *R<sub>f</sub>* values were obtained which are spectroscopically identical not only to each other but also to **5**. These species must be related as diastereoisomers (one racemic, the other meso) but they are indistinguishable. Crystallisations of the two yellow products yielded crystals with the same unit cell dimensions within experimental error as those recorded for **5**.

The reaction between [Ti]<sub>2</sub>[**2**] and [CoCpI<sub>2</sub>(CO)] affords a single isolated species, *rac*-[1-(1'-3'-Cp-3',1',2'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-Cp-3,1,2-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**6**) (Scheme 3). Mass spectrometry and elemental analysis were consistent with both carborane cages having been metalated with {CoCp} fragments. In the <sup>1</sup>H NMR spectrum of **6** is a single resonance for the Cp-*H* atoms and a single resonance assigned to C<sub>cage</sub>*H*, the relatively high frequency of the latter (4.25 ppm) consistent with a 3,1,2-CoC<sub>2</sub>B<sub>9</sub> architecture.<sup>23</sup> The <sup>11</sup>B{<sup>1</sup>H} NMR spectrum is also in accord with a product in which both cages are chemically and magnetically equivalent, with eight discernible resonances from 5.2 to -14.3 ppm.

<Scheme 3 near here>

The structural identity of **6** was confirmed crystallographically (Fig. 10). Both cobaltacarborane cages are present as the 3,1,2-CoC<sub>2</sub>B<sub>9</sub> isomer, with bend-back angles of the Cp rings relative to the cages of 16.61(15) and 15.84(14)° for the unprimed and primed cages, respectively, and significantly longer connectivities from the metal atoms to the cage C atoms bearing the metallacarborane substituents. An approximate (non-crystallographically-imposed) C<sub>2</sub> axis bisects the C1–C1' bond and thus the chirality of both cages is the same, meaning that **6** is the racemic form of [1-(1'-3'-Cp-3',1',2'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-Cp-3,1,2-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>]. Although both racemic and meso forms of this species might be anticipated, given that [Ti]<sub>2</sub>[**2**] exists as a diastereoisomeric mixture, we were only able to isolate *rac*-**6**.

<Fig. 10 near here>

An interesting feature of *rac*-**6** is intramolecular dihydrogen bonding. It is well established that in (hetero)carboranes the *CH* atoms are relatively protonic and the *BH* atoms relatively hydridic. Moreover, in 3,1,2-MC<sub>2</sub>B<sub>9</sub>H<sub>11</sub> compounds whose NMR spectra have been fully assigned,<sup>25</sup> the most shielded (most hydridic) *BH* atoms are H5 (H11) and H6. The racemic arrangement of the two CoC<sub>2</sub>B<sub>9</sub> cages in **6** allows for four intramolecular intercage dihydrogen bonds, *CH2*...*BH5'* 2.43(5) Å, *CH2*...*BH6'* 2.54(5) Å, *CH2'*...*BH5* 2.44(5) Å and *CH2'*...*BH6* 2.37(5) Å<sup>26</sup> (Fig. 11). We note that in the analogous meso isomer (not isolated) the maximum number of such interactions would be two, whatever the rotamer (assuming a staggered arrangement of the two opposing 5-atom faces).

<Fig. 11 near here>

Thermolysis of **II** at toluene reflux yielded no evidence for the formation of an isomerised cobaltacarborane,<sup>13</sup> but, in contrast, heating **6** to reflux in dimethoxyethane for 1 h affords compound **4α** (Scheme 4). In this process the primed cage isomerises from 3',1',2'-CoC<sub>2</sub>B<sub>9</sub> to 2',1',8'-CoC<sub>2</sub>B<sub>9</sub>, an isomerisation most easily visualised by a 120° rotation of either the C1'B4'B5' or C1'B5'B6' triangular faces. We recall that a 3,1,2-MC<sub>2</sub>B<sub>9</sub> to 2,1,8-MC<sub>2</sub>B<sub>9</sub> isomerisation is implicated in the formation of the ruthenacarboranes **3** and cobaltacarboranes **4** from their presumed 3,1,2-MC<sub>2</sub>B<sub>9</sub>-3',1',2'-MC<sub>2</sub>B<sub>9</sub> precursors. The isolation of **4α** from isomerisation of racemic **6** implies that the α forms of compounds **3** and **4** arise from metalation of the racemic diastereoisomers of [HNMe<sub>3</sub>]<sub>2</sub>[**1**] and [Ti]<sub>2</sub>[**2**] and, conversely, the β forms of **3** and **4** arise from the meso precursors.

<Scheme 4 near here>

The singly-metalated species **II** was, however, successfully isomerised by reduction and subsequent oxidation.<sup>13</sup> Addition of two equivalents of sodium naphthalenide to **6** in THF, followed by aerial oxidation, yields a single yellow product identical to the 2,1,8-CoC<sub>2</sub>B<sub>9</sub>-2',1',8'-CoC<sub>2</sub>B<sub>9</sub> species **5** by both <sup>1</sup>H and <sup>11</sup>B{<sup>1</sup>H} NMR spectroscopies. Based on the above arguments it would be reasonable to suggest that this should be the racemic form of **5** but, as has already been discussed, it appears that racemic **5** and meso **5** are indistinguishable spectroscopically. We crystallised the species afforded by redox of **6** but unit cell dimensions are again identical to those of **5** within experimental error.

## Conclusions

Metalation of doubly-deboronated 1,1'-bis(*ortho*-carborane) with {Ru(*p*-cymene)} affords diastereoisomeric 3,1,2-RuC<sub>2</sub>B<sub>9</sub>-2',1',8'-RuC<sub>2</sub>B<sub>9</sub> bis(ruthenacarboranes) derived from racemic and meso forms of the doubly-deboronated precursor. Metalation with {CoCp} fragments generated *in situ* (CoCl<sub>2</sub>/NaCp) yields analogous species but also a small amount of the unique 2,1,8-CoC<sub>2</sub>B<sub>9</sub>-2',1',8'-CoC<sub>2</sub>B<sub>9</sub> isomer. Due to crystallographic disorder of the non-linking cage



C atoms it is impossible to know whether this is the racemic or meso diastereoisomer or a mixture of both forms. Redox of the 3,1,2-CoC<sub>2</sub>B<sub>9</sub>-2',1',8'-CoC<sub>2</sub>B<sub>9</sub> species converts each to 2,1,8-CoC<sub>2</sub>B<sub>9</sub>-2',1',8'-CoC<sub>2</sub>B<sub>9</sub> isomers which cannot be distinguished. Metalation of doubly-deboronated 1,1'-bis(*ortho*-carborane) with preformed {CoCp} (using [CoCpI<sub>2</sub>(CO)]) yields the racemic form of the 3,1,2-CoC<sub>2</sub>B<sub>9</sub>-3',1',2'-CoC<sub>2</sub>B<sub>9</sub> isomer, a compound showing intramolecular dihydrogen bonding. Thermolysis of the 3,1,2-3',1',2' compound affords only one diastereoisomer of 3,1,2-CoC<sub>2</sub>B<sub>9</sub>-2',1',8'-CoC<sub>2</sub>B<sub>9</sub> as expected, whilst redox results in complete isomerisation to the 2,1,8-CoC<sub>2</sub>B<sub>9</sub>-2',1',8'-CoC<sub>2</sub>B<sub>9</sub> form.

## Experimental

### Synthesis

Experiments were performed under dry, oxygen-free, N<sub>2</sub> using standard Schlenk techniques, although subsequent manipulations were sometimes performed in the open laboratory. Solvents for synthesis and work-up were freshly distilled under nitrogen from the appropriate drying agent [THF and 40-60 petroleum ether (petrol), sodium wire: CH<sub>2</sub>Cl<sub>2</sub> (DCM), calcium hydride] and were degassed (3×freeze-pump-thaw cycles) before use. Deuterated solvents for NMR spectroscopy [CDCl<sub>3</sub>, (CD<sub>3</sub>)<sub>2</sub>SO] were stored over 4 Å molecular sieves. Preparative TLC employed 20×20 cm Kieselgel F<sub>254</sub> glass plates and column chromatography used 60 Å silica as the stationary phase. Elemental analyses were conducted using an Exeter CE-440 elemental analyser. NMR spectra at 400.1 MHz (<sup>1</sup>H) or 128.4 MHz (<sup>1</sup>B) were recorded on a Bruker DPX-400 spectrometer at room temperature. Electron impact mass spectrometry (EIMS) was carried out using a Finnigan (Thermo) LCQ Classic ion trap mass spectrometer at the University of Edinburgh. The starting materials 1,1'-bis(*o*-carborane),<sup>3</sup> [RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub><sup>27</sup> and [CoCpI<sub>2</sub>(CO)]<sup>28</sup> were prepared by literature methods or slight variations thereof. All other reagents were supplied commercially.

**[HNMe<sub>3</sub>]<sub>2</sub>[7-(7'-7',8'-nido-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] ([HNMe<sub>3</sub>]<sub>2</sub>[1]) and [BTMA]<sub>2</sub>[7-(7'-7',8'-nido-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-7,8-nido-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] ([BTMA]<sub>2</sub>[1])**

1,1'-Bis(*o*-carborane) (0.50 g, 1.75 mmol) and KOH (2.94 g, 52.4 mmol) were dissolved in EtOH (50 mL) and heated to reflux for 48 h. Following cooling to room temperature CO<sub>2</sub>(g) was passed through the mixture for 10 min. The mixture was filtered and the filtrate evaporated under reduced pressure to afford an oil. This was dissolved in deionised water (30 mL) to yield a clear solution which was split into two equal parts. To one was added an aqueous solution of excess [HNMe<sub>3</sub>][Cl] and to the other an aqueous solution of excess [BTMA][Cl]. Both additions immediately resulted in precipitation of white solids which were collected by filtration, washed with water and dried *in vacuo*.

[HNMe<sub>3</sub>]<sub>2</sub>[7-(7'-7',8'-*nido*-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-7,8-*nido*-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] ([HNMe<sub>3</sub>]<sub>2</sub>[1]). Yield 0.24 g, 0.62 mmol, 71%. C<sub>10</sub>H<sub>42</sub>B<sub>18</sub>N<sub>2</sub> requires: C 31.2, H 10.99, N 7.28. Found: C 31.0, H 11.08, N 7.37%. <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>SO, 400.1 MHz] δ 9.28 (s, 2H, HNMe<sub>3</sub>), 2.78 [(s, 18H, HN(CH<sub>3</sub>)<sub>3</sub>), 1.83 (s, C<sub>cage</sub>H), 1.79 (s, C<sub>cage</sub>H). <sup>11</sup>B{<sup>1</sup>H} NMR [(CD<sub>3</sub>)<sub>2</sub>SO, 128.4 MHz] δ -10.9, -14.8, -15.7, -17.6, -18.5, -20.4, -21.3, -23.8, -24.4, -33.6, -36.6.

[BTMA]<sub>2</sub>[7-(7'-7',8'-*nido*-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>)-7,8-*nido*-C<sub>2</sub>B<sub>9</sub>H<sub>11</sub>] ([BTMA]<sub>2</sub>[1]). Yield 0.37 g, 0.65 mmol, 75%. C<sub>24</sub>H<sub>54</sub>B<sub>18</sub>N<sub>2</sub> requires: C 51.0, H 9.63, N 4.96. Found: C 49.8, H 9.60, N 4.43%. <sup>1</sup>H NMR [(CD<sub>3</sub>)<sub>2</sub>SO, 400.1 MHz] δ 7.53 (br. app. s, 10H, C<sub>6</sub>H<sub>5</sub>), 4.51 (s, 4H, CH<sub>2</sub>), 3.02 (s, 18H, CH<sub>3</sub>), 1.82 (s, C<sub>cage</sub>H), 1.79 (s, C<sub>cage</sub>H). <sup>11</sup>B{<sup>1</sup>H} NMR [(CD<sub>3</sub>)<sub>2</sub>SO, 128.4 MHz] identical to that of [HNMe<sub>3</sub>]<sub>2</sub>[1].

**[Tl]<sub>2</sub>[1-(1'-3',1',2'-*closo*-TlC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3,1,2-*closo*-TlC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] ([Tl]<sub>2</sub>[2])**

Excess KOH (4.81 g, 85.7 mmol) and 1,1'-bis(*o*-carborane) (1.00 g, 3.49 mmol) were dissolved in EtOH (30 mL) and heated to reflux for 18 h. The mixture was cooled and solvent removed under reduced pressure. The resulting solid was dissolved in deionised water (30 mL) and filtered. To the filtrate was added a solution of thallous acetate (5.72 g, 21.7 mmol) in deionised water, resulting in the immediate precipitation of a yellow solid. This was collected by filtration, washed with EtOH (30 mL) then Et<sub>2</sub>O (30 mL) and dried *in vacuo* to afford a fine yellow powder subsequently stored in a foil-covered Schlenk tube. [Tl]<sub>2</sub>[1-(1'-3',1',2'-*closo*-TlC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3,1,2-*closo*-TlC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] ([Tl]<sub>2</sub>[2]). Yield 3.56 g, 3.29 mmol, 94%. C<sub>4</sub>H<sub>20</sub>B<sub>18</sub>Tl<sub>4</sub> requires: C 4.45, H 1.87. Found: C 4.25, H 1.92%.

**α-[1-(8'-2'-(*p*-cymene)-2',1',8'-*closo*-RuC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-(*p*-cymene)-3,1,2-*closo*-RuC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (3α) and β-[1-(8'-2'-(*p*-cymene)-2',1',8'-*closo*-RuC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-(*p*-cymene)-3,1,2-*closo*-RuC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (3β)**

[RuCl<sub>2</sub>(*p*-cymene)]<sub>2</sub> (0.57 g, 0.93 mmol) was added to a frozen suspension of [Tl]<sub>2</sub>[2] (1.00 g, 0.93 mmol) in THF (20 mL) and the reaction mixture allowed to thaw and stir for 24 h. The resulting light-brown suspension was filtered and the filtrate concentrated and purified, first by column chromatography on silica (DCM:petrol, 1:1) and subsequently by TLC (ethyl acetate:petrol, 3:7) to afford two mobile yellow bands.

α-[1-(8'-2'-(*p*-cymene)-2',1',8'-*closo*-RuC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-(*p*-cymene)-3,1,2-*closo*-RuC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (3α). R<sub>f</sub> 0.40. Yield 0.075 g, 0.102 mmol, 11%. C<sub>24</sub>H<sub>48</sub>B<sub>18</sub>Ru<sub>2</sub> requires: C 39.3, H 6.60. Found: C 39.0, H 6.89%. <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400.1 MHz] δ 6.06-5.77 (m, 8H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 3.96 (br s, 1H, C<sub>cage</sub>H), 3.06 (sept, 1H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.80 (sept, 1H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.61 (br s, 1H, C<sub>cage</sub>H), 2.44 (s, 3H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.31 (s, 3H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 1.35-1.26 (m, 12H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR [CDCl<sub>3</sub>, 128.4 MHz] δ 1.7, 0.1, -1.3, -7.7, -8.2, -12.9, -16.8, -21.5. EIMS: envelope centred on *m/z* 733 (M<sup>+</sup>).

$\beta$ -[1-(8'-2'-(*p*-cymene)-2',1',8'-*closo*-RuC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-(*p*-cymene)-3,1,2-*closo*-RuC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**3 $\beta$** ). *R*<sub>f</sub> 0.42. Yield 0.032 g, 0.044 mmol, 5%. C<sub>24</sub>H<sub>48</sub>B<sub>18</sub>Ru<sub>2</sub> requires: C 39.3, H 6.60. Found: C 38.8, H 6.51%. <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400.1 MHz]  $\delta$  6.08-5.78 (m, 8H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 3.79 (br s, 1H, C<sub>cage</sub>H), 3.04 (sept, 1H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.79 (sept, 1H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.58 (br s, 1H, C<sub>cage</sub>H), 2.47 (s, 3H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 2.30 (s, 3H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>), 1.34-1.27 (m, 12H, CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CH(CH<sub>3</sub>)<sub>2</sub>). <sup>11</sup>B{<sup>1</sup>H} NMR [CDCl<sub>3</sub>, 128.4 MHz]  $\delta$  1.7, 0.0, -1.2, -3.8, -4.9, -7.9, -13.1, -16.9, -21.1. EIMS: envelope centred on *m/z* 733 (M<sup>+</sup>).

NB. In this and the following metalation reactions isolated yields of products (following purification involving both column and preparative thin-layer chromatography) are relatively low. Following chromatography, non-mobile components removed from silica with MeCN have <sup>11</sup>B NMR spectra which typically include resonances between -30 and -40 ppm characteristic of 7,8-*nido*-C<sub>2</sub>B<sub>9</sub> fragments, so we ascribe the low yields of metallacarborane products to poor conversion as opposed to decomposition.

$\alpha$ -[1-(8'-2'-Cp-2',1',8'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-Cp-3,1,2-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**4 $\alpha$** ),  $\beta$ -[1-(8'-2'-Cp-2',1',8'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-Cp-3,1,2-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**4 $\beta$** ) and [8-(8'-2'-Cp-2',1',8'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-2-Cp-2,1,8-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**5**)

(a) From [HNMe<sub>3</sub>]<sub>2</sub>[**1**]

To [HNMe<sub>3</sub>]<sub>2</sub>[**1**] (0.20 g, 0.52 mmol) suspended in THF (20 mL) 0 °C was added *n*-BuLi (0.92 mL of 2.5M solution in hexanes, 2.29 mmol) and the cloudy white product heated to reflux for 2 h. This was then frozen and NaCp (1.65 mL of a 2M solution in hexanes, 3.30 mmol) and CoCl<sub>2</sub> (0.47 g, 3.62 mmol) added. Following warming to room temperature and stirring for 18 h the mixture was aerielly oxidised for 0.5 h. THF was removed *in vacuo* and the crude mixture dissolved in DCM and filtered through silica. Preparative TLC yielded orange (*R*<sub>f</sub> 0.24), orange (*R*<sub>f</sub> 0.45) and yellow (*R*<sub>f</sub> 0.61) bands subsequently identified as **4 $\alpha$** , **4 $\beta$**  and **5**, in yields of 0.016 g (0.03 mmol, 6%), 0.010 g (0.02 mmol, 4%) and 0.007 g (0.01 mmol, 3%), respectively.

(b) From [Ti]<sub>2</sub>[**2**]

To a frozen suspension of [Ti]<sub>2</sub>[**2**] (1.40 g, 1.30 mmol) in THF (20 mL) was added CoCl<sub>2</sub> (1.18 g, 9.09 mmol) and NaCp (3.95 mL of a 2M solution in hexanes, 7.90 mmol). The mixture was allowed to warm to room temperature and stirred for 24 h, following which it was aerielly oxidised for 1 h. The reagents were filtered and the filtrate concentrated and purified by column chromatography on silica (DCM:petrol, 1:1) affording a mobile orange band which was further purified by preparative TLC (ethyl acetate:petrol, 3:7) to afford two orange bands subsequently identified as **4 $\alpha$**  (*R*<sub>f</sub> 0.24) and **4 $\beta$**  (*R*<sub>f</sub> 0.43) in yields of 0.090 g (0.18 mmol, 14%) and 0.077 g (0.15 mmol, 12%), respectively.

$\alpha$ -[1-(8'-2'-Cp-2',1',8'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-Cp-3,1,2-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**4 $\alpha$** ). C<sub>14</sub>H<sub>30</sub>B<sub>18</sub>Co<sub>2</sub> requires: C 32.9, H 5.92. Found: C 32.8, H 5.96%. <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400.1 MHz]  $\delta$  5.79 (s,

5H, C<sub>5</sub>H<sub>5</sub>), 5.48 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.20 (br s, 1H, C<sub>cage</sub>H), 2.76 (br s, 1H, C<sub>cage</sub>H). <sup>11</sup>B{<sup>1</sup>H} NMR [CDCl<sub>3</sub>, 128.4 MHz] δ 5.5, 2.5, 1.7, -1.4, -3.7, -8.5, -10.2, -12.0, -14.6, -15.8, -18.2. EIMS: envelope centred on *m/z* 511 (M<sup>+</sup>).

β-[1-(8'-2'-Cp-2',1',8'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-Cp-3,1,2-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**4β**). C<sub>14</sub>H<sub>30</sub>B<sub>18</sub>Co<sub>2</sub> requires: C 32.9, H 5.92. Found: C 33.1, H 6.01%. <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400.1 MHz] δ 5.80 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 5.47 (s, 5H, C<sub>5</sub>H<sub>5</sub>), 4.06 (br s, 1H, C<sub>cage</sub>H), 2.76 (br s, 1H, C<sub>cage</sub>H). <sup>11</sup>B{<sup>1</sup>H} NMR [CDCl<sub>3</sub>, 128.4 MHz] δ 5.4, 2.4, 1.7, -1.7, -3.8, -8.5, -10.4, -12.3, -14.6, -18.2. EIMS: envelope centred on *m/z* 511 (M<sup>+</sup>).

[8-(8'-2'-Cp-2',1',8'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-2-Cp-2,1,8-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**5**). C<sub>14</sub>H<sub>30</sub>B<sub>18</sub>Co<sub>2</sub> requires: C 32.9, H 5.92. Found: C 32.2, H 5.86%. <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400.1 MHz] δ 5.41 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 2.66 (br s, 2H, C<sub>cage</sub>H). <sup>11</sup>B{<sup>1</sup>H} NMR [CDCl<sub>3</sub>, 128.4 MHz] δ 1.1, -0.9 (combined integral 8B), -5.7 (4B), -12.0 (2B), -16.8, -18.0 (combined integral 4B). EIMS: envelope centred on *m/z* 511 (M<sup>+</sup>).

**Redox isomerisations of 4α and 4β.** To a frozen solution of **4α** (0.02 g, 0.04 mmol) in THF (10 mL) was added a solution of sodium naphthalenide (1 mL of a 0.078 M solution in THF, 0.078 mmol). The reaction was allowed to warm and stir under nitrogen for 16 h and was then aerielly oxidised for 0.5 h. Purification by preparative TLC (ethyl acetate:petrol, 3:7) afforded orange **4α** (*R<sub>f</sub>* 0.24, 0.014 g, 0.03 mmol, 69%) and a yellow product (*R<sub>f</sub>* 0.59, 0.004 g, 0.01 mmol, 20%) identical to **5** by <sup>1</sup>H and <sup>11</sup>B{<sup>1</sup>H} NMR spectroscopies and mass spectrometry. Similarly, from of **4β** (0.010 g, 0.020 mmol) in THF (10 mL) and sodium naphthalenide (0.5 mL of a 0.078 M solution in THF, 0.039 mmol) were recovered orange **4β** (*R<sub>f</sub>* 0.43, 0.006 g, 0.01 mmol, 58%) and a yellow product (*R<sub>f</sub>* 0.57, 0.003 g, 0.01 mmol, 29%) which was again identical to **5** by <sup>1</sup>H and <sup>11</sup>B{<sup>1</sup>H} NMR spectroscopies and mass spectrometry.

***rac*-[1-(1'-3'-Cp-3',1',2'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-Cp-3,1,2-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**6**)**

To a frozen suspension of [Ti]<sub>2</sub>[**2**] (1.00 g, 0.93 mmol) in THF (20 mL) was added [CoCpI<sub>2</sub>(CO)] (0.76 g, 1.87 mmol) and the reaction mixture allowed to thaw and stir for 24 h. The resulting dark suspension was filtered through Celite® and solvent removed *in vacuo*. Purification by preparative TLC (ethyl acetate:petrol, 3:7) afforded *rac*-[1-(1'-3'-Cp-3',1',2'-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>)-3-Cp-3,1,2-*closo*-CoC<sub>2</sub>B<sub>9</sub>H<sub>10</sub>] (**6**) as an orange solid (*R<sub>f</sub>* 0.48, 0.068 g, 0.13 mmol, 14%). C<sub>14</sub>H<sub>30</sub>B<sub>18</sub>Co<sub>2</sub> requires: C 32.9, H 5.92. Found: C 32.2, H 5.73%. <sup>1</sup>H NMR [CDCl<sub>3</sub>, 400.1 MHz] δ 5.84 (s, 10H, C<sub>5</sub>H<sub>5</sub>), 4.24 (br s, 2H, C<sub>cage</sub>H). <sup>11</sup>B{<sup>1</sup>H} NMR [CDCl<sub>3</sub>, 128.4 MHz] δ 5.2 (2B), 1.2 (2B), -2.5, -3.3 (combined integral 6B), -7.6 (2B), -11.7, -13.2, -14.2 (combined integral 6B). EIMS: envelope centred on *m/z* 511 (M<sup>+</sup>).

**Thermal isomerisation of 6.** Compound **6** (0.02 g, 0.04 mmol) was dissolved in dimethoxyethane (15 mL) and the orange solution heated at reflux for 1 h. The solvent was

removed and the crude residue subjected to preparative TLC (ethyl acetate:petrol, 3:7) affording two orange bands at  $R_f$  0.51 and  $R_f$  0.25, identified as **6** (0.003 g, 0.01 mmol, 15%) and **4 $\alpha$**  (0.012 g, 0.02 mmol, 60%), respectively, by  $^1\text{H}$  and  $^{11}\text{B}\{^1\text{H}\}$  NMR spectroscopies.

**Redox isomerisation of 6.** To a frozen solution of **6** (0.025 g, 0.05 mmol) in THF (10 mL) was added sodium naphthalenide (2 mL of a 0.049M solution in THF, 0.098 mmol). The reaction was allowed to warm and stir under nitrogen for 16 h and was then aerielly oxidised for 0.5 h. Purification by preparative TLC (ethyl acetate:petrol, 3:7) afforded a yellow product ( $R_f$  0.58, 0.007 g, 0.01 mmol, 28%) identical to **5** by  $^1\text{H}$  and  $^{11}\text{B}\{^1\text{H}\}$  NMR spectroscopies.

## Crystallography

Diffraction-quality crystals of  $[\text{BTMA}]_2[\mathbf{1}]$ , **3 $\beta$**  and **4 $\beta$**  were grown by slow diffusion of petrol and a DCM solution of the appropriate compound. Crystals of **4 $\beta$** ·MeCN and **6**·MeCN were also grown by solvent diffusion, this time using MeCN as solvent and diethylether as antisolvent. Compound **4 $\alpha$**  afforded crystals by vapour diffusion between a THF solution of the compound and petrol. Finally, crystals of **3 $\alpha$**  and **5** were grown by slow evaporation of a  $\text{d}_6$ -acetone solution and a DCM solution, respectively. Except for **3 $\alpha$**  and **5**, intensity data were collected on a Bruker X8 APEXII diffractometer using  $\text{Mo-K}\alpha$  X-radiation, with crystals mounted in inert oil on a cryoloop and cooled to 100 K by an Oxford Cryosystems Cryostream. Data from **3 $\alpha$**  were obtained at 120 K and data from **5** at 100 K by the National Crystallography Service at the University of Southampton. Indexing, data collection and absorption correction were performed using the APEXII suite of programs.<sup>29</sup> Using OLEX2<sup>30</sup> structures were solved by direct methods using the SHELXS<sup>31</sup> or SHELXT<sup>32</sup> programme and refined by full-matrix least-squares (SHELXL).<sup>31</sup>

All crystals were single except those of **3 $\alpha$** , **4 $\alpha$**  and **4 $\beta$** ·MeCN, each of which was treated as a two-component twin. All crystals were also fully ordered except those of  $[\text{BTMA}]_2[\mathbf{1}]$ , **3 $\alpha$** , **3 $\beta$**  and **5**. In  $[\text{BTMA}]_2[\mathbf{1}]$  there is C:B disorder between vertices 8 and 11 of the nido carborane cages (arising from the presence of two diastereoisomers) and also partial disorder of both vertices into the 12<sup>th</sup> vertex of a closo icosahedron affording a ‘ghost’ vertex. **3 $\alpha$**  and **3 $\beta$**  each suffer from partial disorder of one *p*-cymene ligand, but in all three disordered structures the disorder was satisfactorily modelled. In **5** vertices 1 and 11 (and 1' and 11') are required to be 50%C+50%B by space group symmetry.

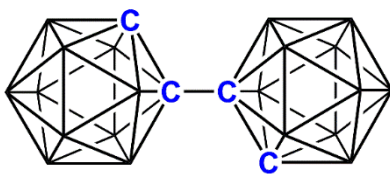
Cage C atoms bearing only H substituents were distinguished from B atoms by the VCD<sup>33</sup> and BHD<sup>34</sup> methods (in the case of  $[\text{BTMA}]_2[\mathbf{1}]$  the VCD method helped to identify the disorder between vertices 8 and 11). For all structures H atoms bound to cage B or cage C atoms were allowed to refine positionally whilst H atoms bound to other C atoms were constrained to idealised geometries;  $\text{C}_{\text{phenyl}}\text{--H} = 0.95 \text{ \AA}$ ,  $\text{C}_{\text{primary}}\text{--H} = 0.98 \text{ \AA}$ ,  $\text{C}_{\text{secondary}}\text{--H} = 0.99$

Å, C<sub>tertiary</sub>-H = 1.00 Å, C<sub>π-bonded</sub>-H = 1.00 Å. All H displacement parameters,  $U_{\text{iso}}$ , were constrained to be  $1.2 \times U_{\text{eq}}$  (bound B or C) except Me H atoms [ $U_{\text{iso}}(\text{H}) = 1.5 \times U_{\text{eq}} \text{C}(\text{Me})$ ]. Table 1 contains further experimental details.

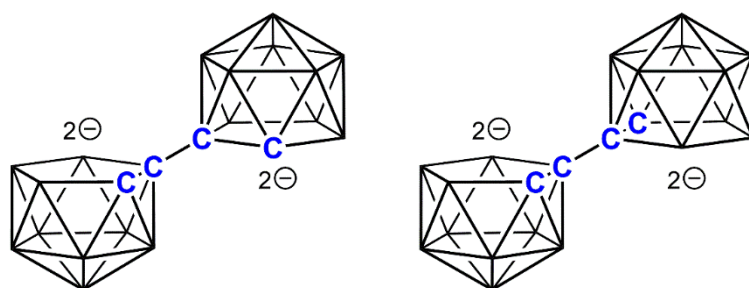
<Table 1 near here>

## Acknowledgements

We thank ORSAS (GT), Heriot-Watt University (DM, James Watt Studentship) and the EPSRC (WYM, grant EP/I031545/1) for support, and the National Crystallography Service (University of Southampton) for data collection from compounds **3α** and **5**. MA is an Erasmus exchange student from the Phillips-Universität Marburg, Germany.

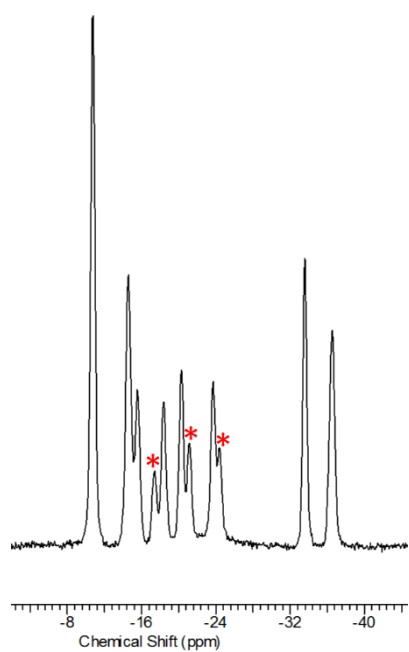


**Fig. 1** 1,1'-bis(*ortho*-carborane).

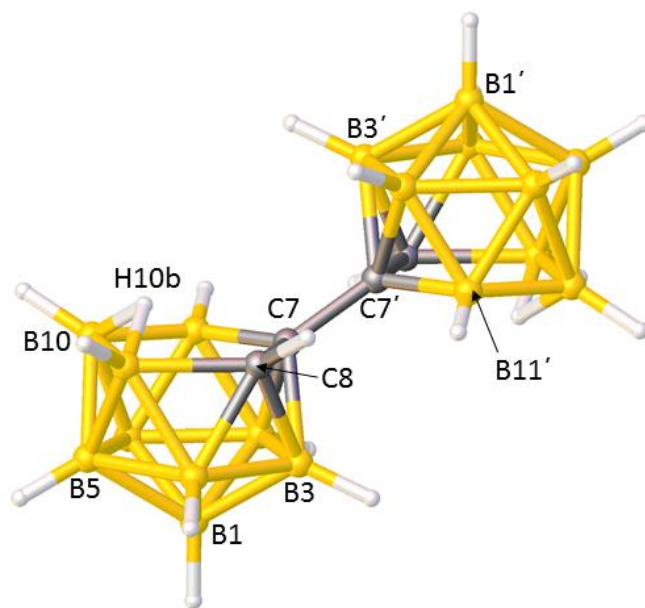


**Fig. 2** Racemic (left) and meso (right) forms of doubly-deboronated 1,1'-bis(*ortho*-carborane).

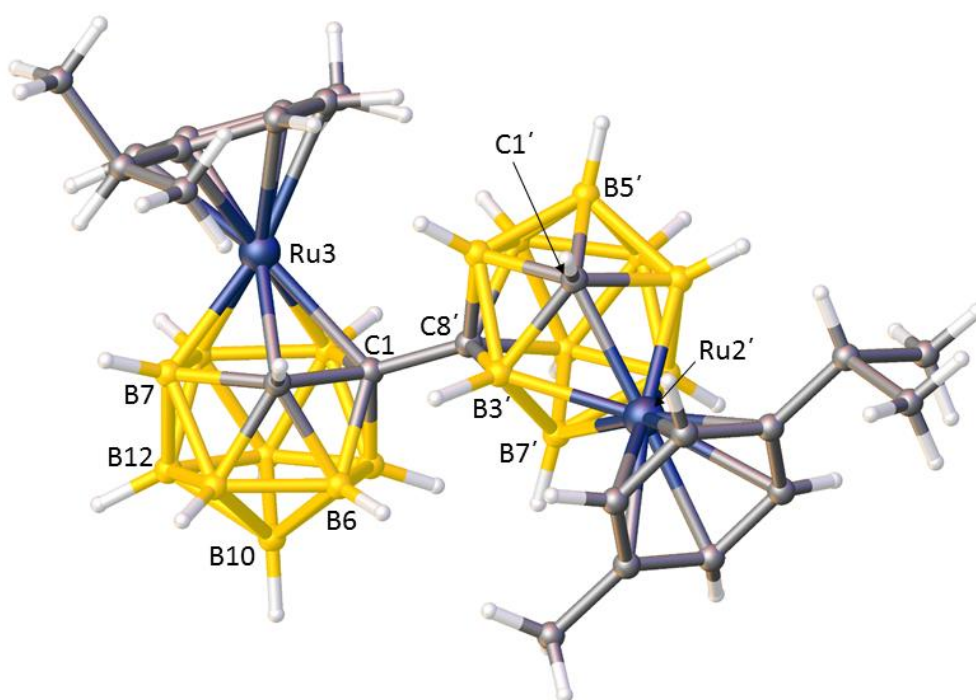




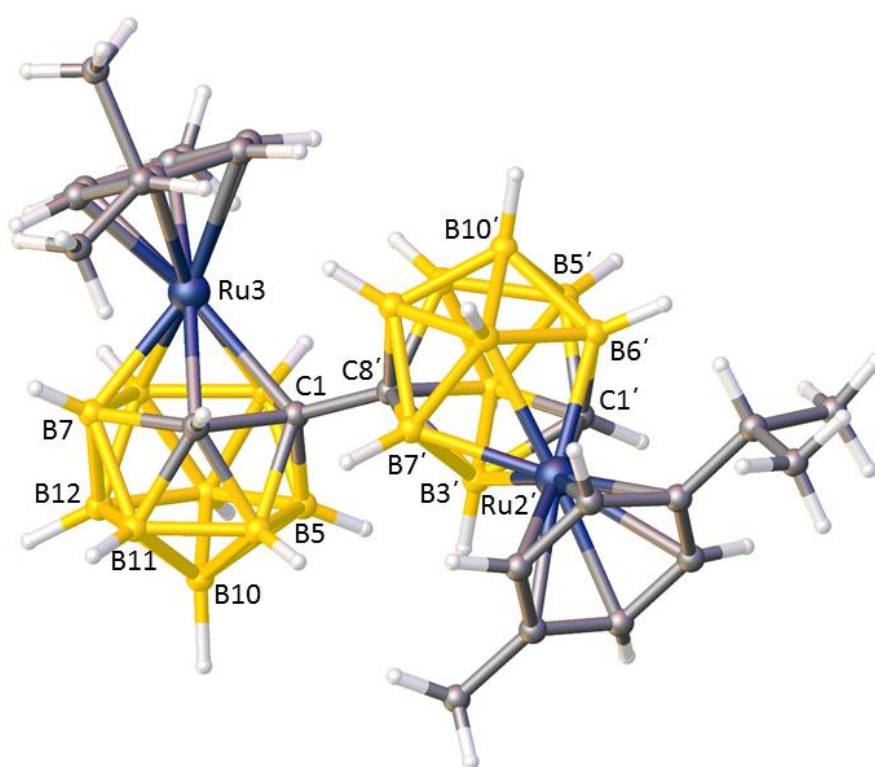
**Fig. 3** The 128.4 MHz  $^{11}\text{B}\{^1\text{H}\}$  NMR spectrum of  $[\text{HNMe}_3]_2[\mathbf{1}]$  in  $(\text{CD}_3)_2\text{SO}$  (that of  $[\text{BTMA}]_2[\mathbf{1}]$  is identical) showing (asterisks) minor resonances consistent with the sample being a mixture of diastereoisomers.



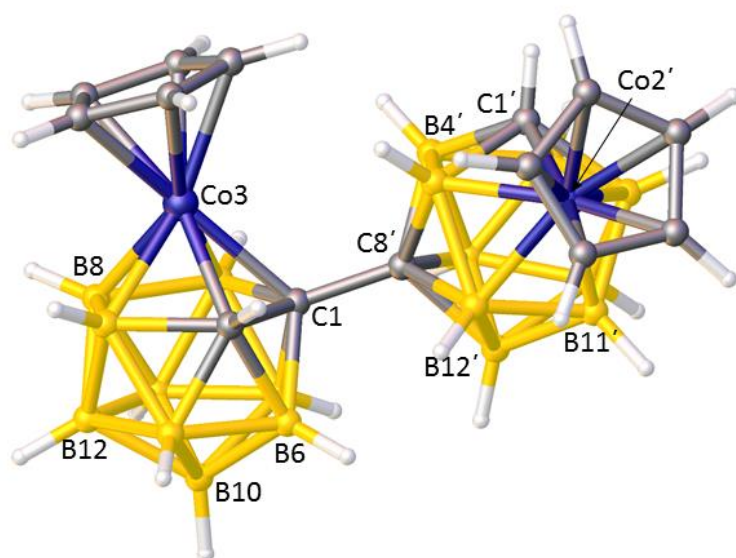
**Fig. 4** View of the major (meso) component of the disordered anion in [BTMA]<sub>2</sub>[**1**]. There is a crystallographic inversion centre at the mid-point of the C7–C7' bond. C7–C7' 1.517(3) Å.



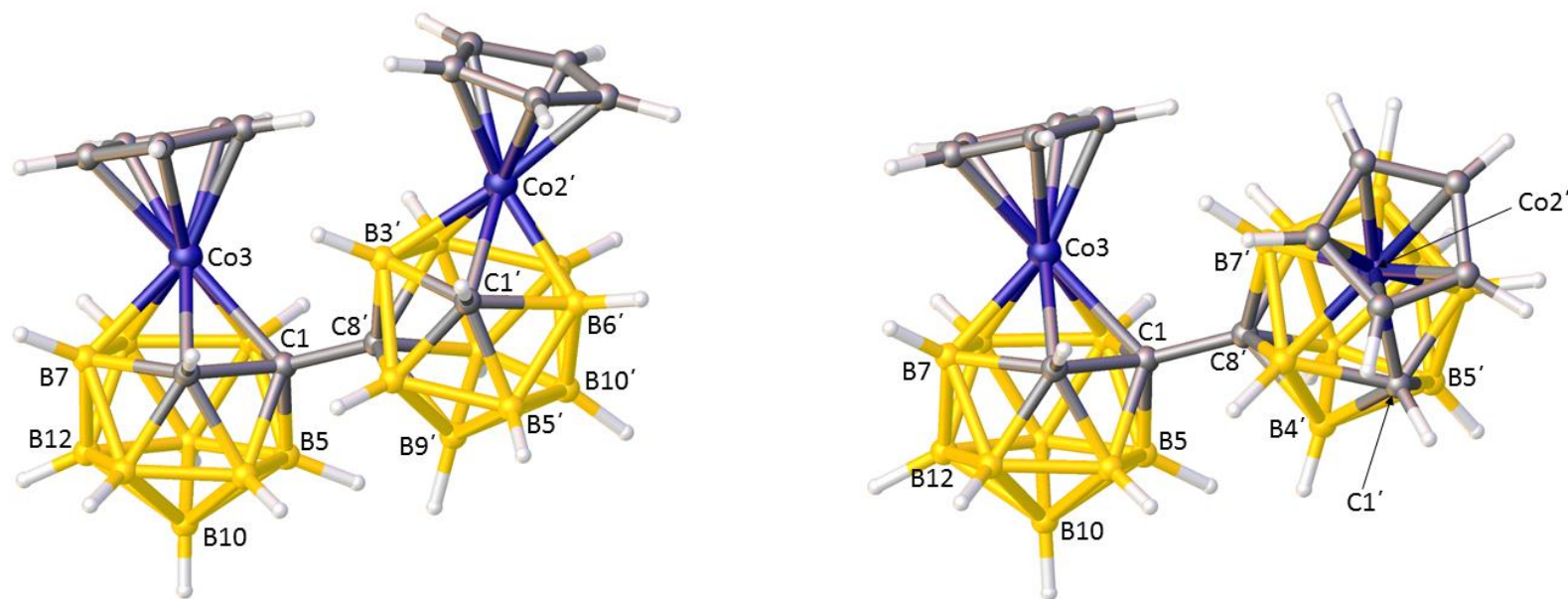
**Fig. 5** Perspective view of compound **3α** with atomic numbering scheme. Only the major component of the disordered *p*-cymene ligand on Ru2' is shown for clarity. Selected interatomic distances (Å): Ru3–C1 2.302(6), Ru3–C2 2.199(6), C1–C2 1.650(9), Ru2'–C1' 2.176(7), C1–C8' 1.546(8).



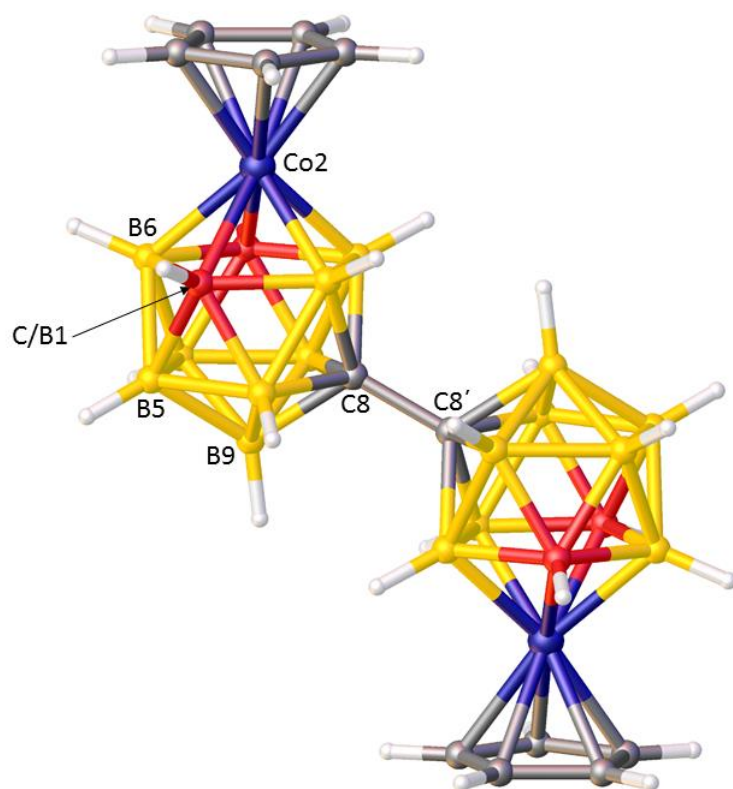
**Fig. 6** Perspective view of compound **3β** with atomic numbering scheme. Only the major component of the disordered *p*-cymene ligand on Ru3 is shown for clarity. Selected interatomic distances (Å): Ru3–C1 2.292(7), Ru3–C2 2.200(8), C1–C2 1.634(10), Ru2'–C1' 2.177(7), C1–C8' 1.555(9).



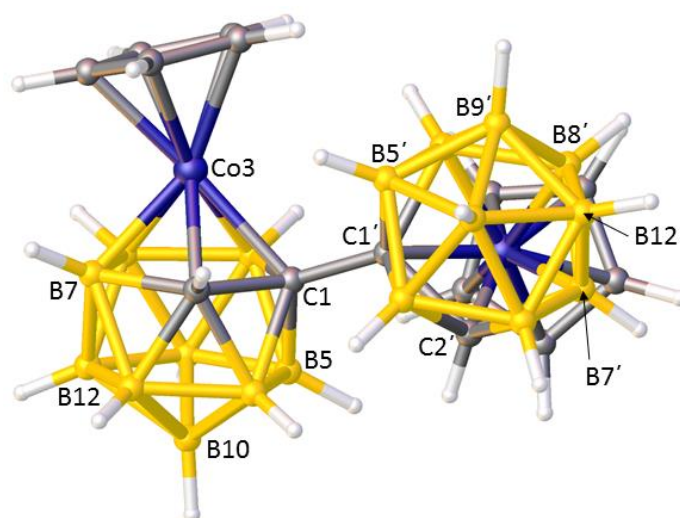
**Fig. 7** Perspective view of compound **4 $\alpha$**  with atomic numbering scheme. Selected interatomic distances (Å): Co3–C1 2.141(3), Co3–C2 2.051(3), C1–C2 1.640(4), Co2'–C1' 2.020(3), C1–C8' 1.551(4).



**Fig. 8** Two views of compound **4β**. Left is the structure determined from crystals afforded from DCM:petrol and right that afforded from MeCN:Et<sub>2</sub>O (MeCN of solvation not shown). The two structures are related by a rotation of *ca.* 72° about the C1–C8' bond. Selected interatomic distances (Å; left structure in normal text, right structure in italics): Co3–C1 2.127(3), *2.134(8)*; Co3–C2 2.039(3), *2.050(8)*; C1–C2 1.651(5), *1.670(10)*; Co2'–C1' 2.022(3), *2.005(8)*; C1–C8' 1.552(4), *1.549(10)*.

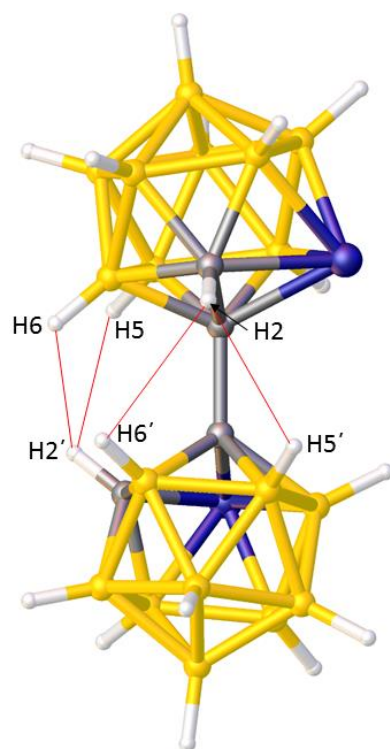


**Fig. 9** Perspective view of compound **5** with atomic numbering scheme. The molecule has crystallographically-imposed  $C_{2h}$  ( $2/m$ ) symmetry with the  $C_2$  axis bisecting the C8–C8' bond and the mirror plane in the plane of the paper. Atoms shown in red are disordered, 50%C+50%B. Selected interatomic distances (Å): Co2–C/B1 2.0423(13), Co2–B3 2.0329(13), Co2–B6 2.0440(19), C8–C8' 1.534(3).

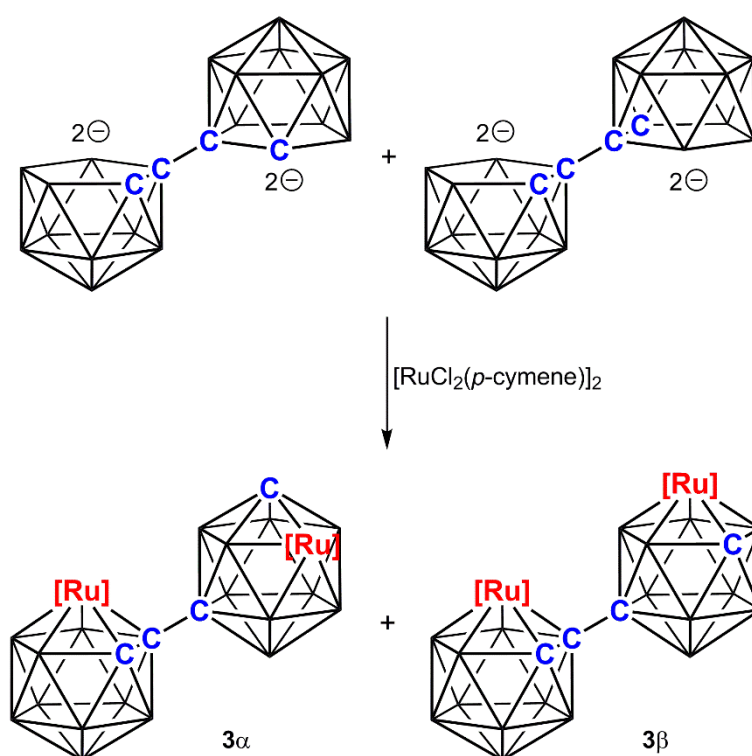


**Fig. 10** Perspective view of compound **6** with atomic numbering scheme. Note that only the racemic diastereoisomers of this species was isolated. Selected interatomic distances ( $\text{\AA}$ ): Co3–C1 2.140(3), Co3–C2 2.049(3), C1–C2 1.668(4), Co3'–C1' 2.135(3), Co3'–C2' 2.043(3), C1'–C2' 1.664(5), C1–C1' 1.563(5).

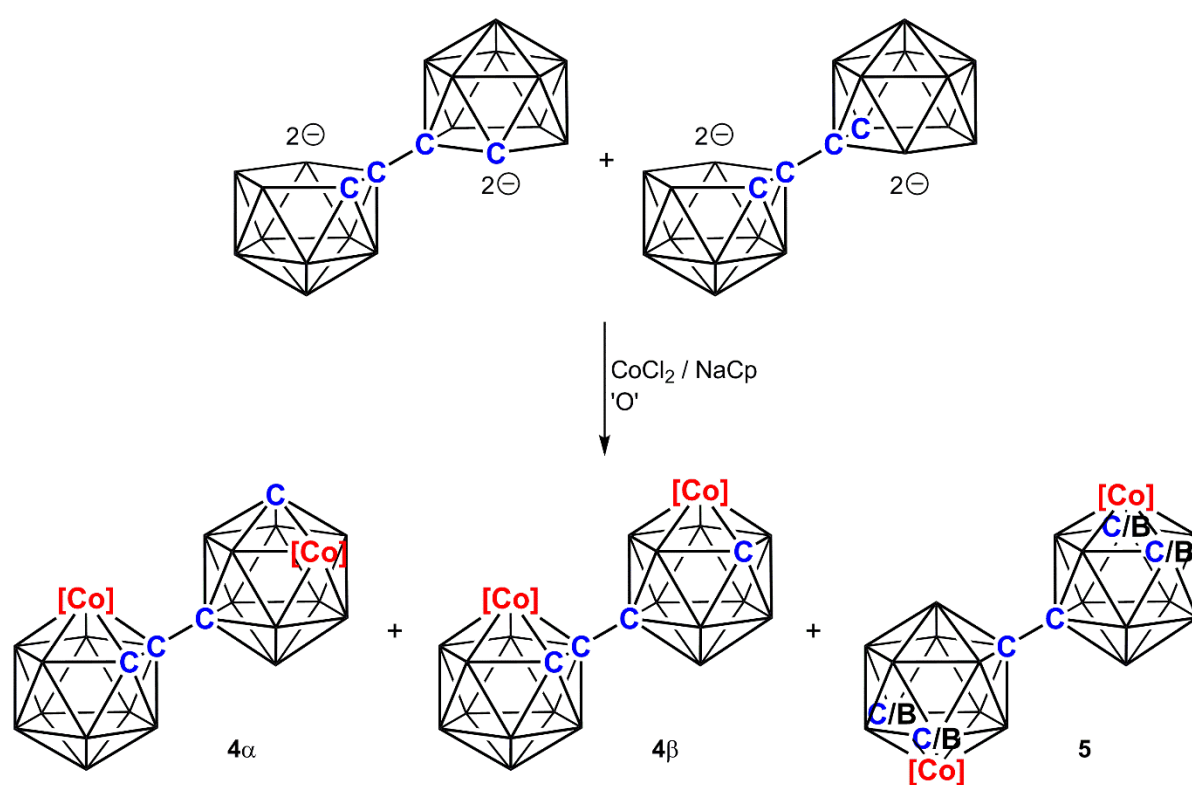




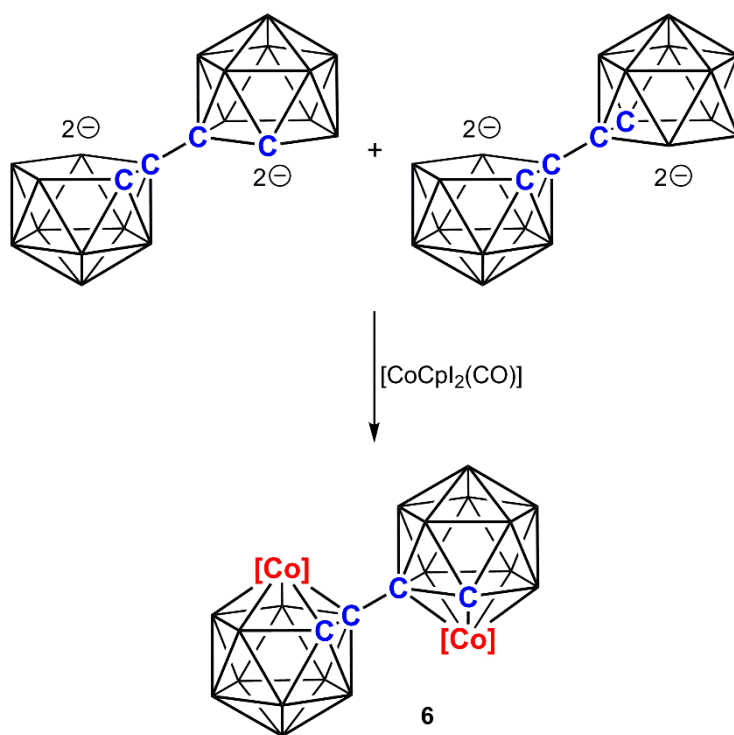
**Fig. 11** View of compound **6** demonstrating intramolecular dihydrogen bonding (red lines). Cp ligands have been omitted for clarity. Distances (Å):  $CH2 \cdots BH5'$  2.43(5),  $CH2 \cdots BH6'$  2.54(5),  $CH2' \cdots BH5$  2.44(5),  $CH2' \cdots BH6$  2.37(5).



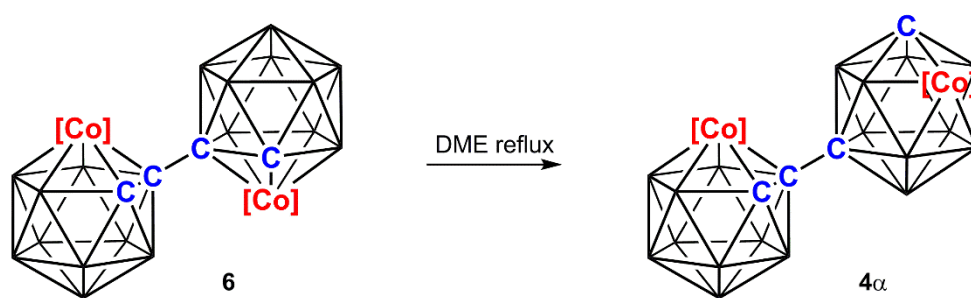
**Scheme 1** Synthesis of ruthenacarboranes  $3\alpha$  and  $3\beta$  from either  $[\text{HNMe}_3]_2[\mathbf{1}]$  or  $[\text{Ti}]_2[\mathbf{2}]$ .  
 $[\text{Ru}] = \{\text{Ru}(p\text{-cymene})\}$ .



**Scheme 2** Synthesis of cobaltacarboranes **4α**, **4β** and **5** from  $[\text{HNMe}_3]_2[\mathbf{1}]$ . Using  $[\text{Tl}]_2[\mathbf{2}]$  as the source of the carborane leads to isolation of only **4α** and **4β**.  $[\text{Co}] = \{\text{CoCp}\}$ .



**Scheme 3** Synthesis of the racemic cobaltacarborane **6** from reaction between  $[\text{Ti}]_2[\mathbf{2}]$  and  $[\text{CoCpI}_2(\text{CO})]$ .  $[\text{Co}] = \{\text{CoCp}\}$ .



**Scheme 4** Thermal isomerisation of **6** to afford **4 $\alpha$** . [Co] = {CoCp}.

**Table 1** Crystallographic data

	[BTMA] <sub>2</sub> [1]	3 $\alpha$	3 $\beta$	4 $\alpha$	4 $\beta$	4 $\beta$ ·MeCN	5	6·MeCN
CCDC	1516771	1516772	1516773	1516774	1516775	1516776	1516777	1516778
Formula	C <sub>24</sub> H <sub>54</sub> B <sub>18</sub> N <sub>2</sub>	C <sub>24</sub> H <sub>48</sub> B <sub>18</sub> Ru <sub>2</sub>	C <sub>24</sub> H <sub>48</sub> B <sub>18</sub> Ru <sub>2</sub>	C <sub>14</sub> H <sub>30</sub> B <sub>18</sub> Co <sub>2</sub>	C <sub>14</sub> H <sub>30</sub> B <sub>18</sub> Co <sub>2</sub>	C <sub>16</sub> H <sub>33</sub> B <sub>18</sub> Co <sub>2</sub> N	C <sub>14</sub> H <sub>30</sub> B <sub>18</sub> Co <sub>2</sub>	C <sub>16</sub> H <sub>33</sub> B <sub>18</sub> Co <sub>2</sub> N
<i>M</i>	565.27	733.34	733.34	510.82	510.82	551.87	510.82	551.87
Crystal system	triclinic	monoclinic	monoclinic	monoclinic	monoclinic	orthorhombic	orthorhombic	monoclinic
Space group	<i>P</i> bar1	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>Cmce</i>	<i>Cc</i>
<i>a</i> / Å	8.8436(12)	9.3011(6)	19.190(2)	7.5433(8)	11.6962(13)	8.9085(6)	11.6943(5)	10.5603(5)
<i>b</i> / Å	10.5897(11)	41.899(3)	10.7869(11)	14.3480(12)	15.9743(17)	13.5333(10)	13.8151(5)	26.9574(12)
<i>c</i> / Å	11.103(2)	9.3950(6)	17.9357(17)	21.5040(17)	12.9143(13)	20.8343(16)	14.4745(6)	9.0101(4)
$\alpha$ / °	116.225(6)	90	90	90	90	90	90	90
$\beta$ / °	101.483(7)	113.751(2)	116.289(4)	96.906(4)	109.935(4)	90	90	97.611(3)
$\gamma$ / °	104.113(5)	90	90	90	90	90	90	90
<i>U</i> / Å <sup>3</sup>	846.5(2)	3351.2(4)	3328.8(6)	2310.5(4)	2268.3(4)	2511.8(3)	2338.47(17)	2542.4(2)
<i>Z</i> , <i>Z'</i>	1, 0.5	4, 1	4, 1	4, 1	4, 1	4, 1	4, 0.25	4, 1
<i>F</i> (000) /e	302	1480	1480	1032	1032	1120	1032	1120
<i>D</i> <sub>calc</sub> / Mg m <sup>-3</sup>	1.109	1.454	1.463	1.448	1.496	1.459	1.451	1.442
$\mu$ (Mo-K $\alpha$ ) / mm <sup>-1</sup>	0.055	0.920	0.926	1.440	1.467	1.332	1.423	1.316
$\theta_{\max}$ / °	28.34	25.69	26.15	27.08	25.99	25.76	27.57	30.03
Data measured	11069	18710	42726	35422	19160	26419	13750	25633
Unique data, <i>n</i>	4082	6370	6592	5094	4434	2873	1399	7256
<i>R</i> <sub>int</sub>	0.0332	0.0647	0.1180	0.0540	0.0757	0.0860	0.0274	0.0483
<i>R</i> , w <i>R</i> <sub>2</sub> (obs. data)	0.0495, 0.1184	0.0657, 0.1228	0.0613, 0.1431	0.0371, 0.0748	0.0457, 0.1105	0.0571, 0.0866	0.0216, 0.0585	0.0352, 0.0633
<i>S</i>	1.026	1.276	1.011	1.046	1.014	1.032	1.087	0.984
Variables	247	475	488	368	367	396	101	395
<i>E</i> <sub>max</sub> , <i>E</i> <sub>min</sub> / e Å <sup>-3</sup>	0.29, -0.23	1.21, -1.17	1.52, -1.89	0.40, -0.45	1.03, -1.04	0.58, -0.56	0.37, -0.26	0.68, -0.36
Abs. str. parameter						0.34(3)		0.022(8)

## References

1. W. Y. Man, G. M. Rosair and A. J. Welch, *Acta Cryst.*, 2014, **E70**, 462.
2. J. A. Dupont and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1964, **86**, 1643.
3. S. Ren and Z. Xie, *Organometallics*, 2008, **27**, 5167.
4. M. J. Martin, W. Y. Man, G. M. Rosair and A. J. Welch, *J. Organomet. Chem.*, 2015, **798**, 36.
5. Z.-J. Yao, Y.-Y. Zhang and G.-X. Jin, *J. Organomet. Chem.*, 2015, **798**, 274.
6. G. S. Kazakov, I. B. Sivaev, K. Yu. Suponitsky, D. D. Kirilin, V. I. Bregadze and A. J. Welch, *J. Organomet. Chem.*, 2016, **806**, 1.
7. S. L. Powley, L. Schaefer, W. Y. Man, D. Ellis, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2016, **45**, 3635.
8. D. Zhao, J. Zhang, Z. Lin and Z. Xie, *Chem. Commun.*, 2016, **52**, 9992.
9. D. Ellis, G. M. Rosair and A. J. Welch, *Chem. Commun.*, 2010, **46**, 7394.
10. D. Mandal, W. Y. Man, G. M. Rosair and A. J. Welch, *Acta Cryst.*, 2015, **C71**, 793.
11. W. Y. Man, D. Ellis, G. M. Rosair and A. J. Welch, *Angew. Chem. Int. Ed.*, 2016, **55**, 4596.
12. W. Y. Man, S. Zlatogorsky, H. Tricas, D. Ellis, G. M. Rosair and A. J. Welch, *Angew. Chem. Int. Ed.*, 2014, **53**, 12222.
13. G. Thiripuranathar, W. Y. Man, C. Palmero, A. P. Y. Chan, B. T. Leube, D. Ellis, D. McKay, S. A. Macgregor, L. Jourdan, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2015, **44**, 5628.
14. D. Mandal, W. Y. Man, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2016, **45**, 15013.
15. D. Ellis, D. McKay, S. A. Macgregor, G. M. Rosair and A. J. Welch, *Angew. Chem. Int. Ed.*, 2010, **49**, 4943.
16. L. E. Riley, A. P. Y. Chan, J. Taylor, W. Y. Man, D. Ellis, G. M. Rosair, A. J. Welch and I. B. Sivaev, *Dalton Trans.*, 2016, **45**, 1127.
17. Y. O. Wong, M. D. Smith and D. V. Peryshkov, *Chem. Eur. J.*, 2016, **22**, 6764.
18. Y. O. Wong, M. D. Smith and D. V. Peryshkov, *Chem. Commun.*, 2016, **52**, 12710.
19. K. O. Kirlikovali, J. C. Axtell, A. Gonzalez, A. C. Phung, S. I. Khan and A. M. Spokoyny, *Chem. Sci.*, 2016, **7**, 5132.
20. P. E. Behnken, T. B. Marder, R. T. Baker, C. B. Knobler, M. R. Thompson and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1985, **107**, 932.
21. M. F. Hawthorne, D. A. Owen and J. W. Wiggins, *Inorg. Chem.*, 1971, **10**, 1034.
22. M. J. Manning, C. B. Knobler, M. F. Hawthorne and Y. Do, *Inorg. Chem.*, 1991, **30**, 3589.

23. M. F. Hawthorne, D. C. Young, T. D. Andrews, D. V. Howe, R. L. Pilling, A. D. Pitts, M. Reintjes, L. F. Warren, Jr. and P. A. Wegner, *J. Am. Chem. Soc.*, 1968, **90**, 879.
24. The overall stereochemistries of **3 $\alpha$**  and **4 $\alpha$**  are the same, as are those of **3 $\beta$**  and **4 $\beta$** .
25. e.g. M. Bown, J. Plešek, K. Baše, B. Štibr, X. L. R. Fontaine, N. N. Greenwood and J. D. Kennedy, *Mag. Res. Chem.*, 1989, **27**, 947.
26. These are the H $\cdots$ H distances as measured by X-ray diffraction. However, because of the systematic underestimation of A–H distances by this technique, true internuclear H $\cdots$ H distances are likely to be somewhat shorter.
27. M. A. Bennett, T.-N. Huang, T. W. Matheson and A. K. Smith, *Inorg. Synth.*, 1982, **21**, 74.
28. S. A. Frith and J. L. Spencer, *Inorg. Synth.*, 1990, **28**, 273.
29. *Bruker AXS APEX2, version 2009-5*, Bruker AXS Inc., Madison, Wisconsin, USA, 2009.
30. O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Cryst.*, 2009, **42**, 339.
31. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
32. G. M. Sheldrick, *Acta Cryst.*, 2015, **A71**, 3.
33. A. McAnaw, G. Scott, L. Elrick, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2013, **42**, 645.
34. A. McAnaw, M. E. Lopez, D. Ellis, G. M. Rosair and A. J. Welch, *Dalton Trans.*, 2014, **43**, 5095.